(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 357 789 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(21) Application number: 89902299.0

(51) Int. Cl.⁵: C04B 38/00 , C04B 35/64

(22) Date of filing: 10.02.89

(86) International application number: PCT/JP89/00139

(87) International publication number: WO 89/07584 (24.08.89 89/20)

(30) Priority: 10.02.88 JP 27616/88

(43) Date of publication of application: 14.03.90 Bulletin 90/11

(84) Designated Contracting States: AT BE CH DE FR GB IT LI LU NL SE

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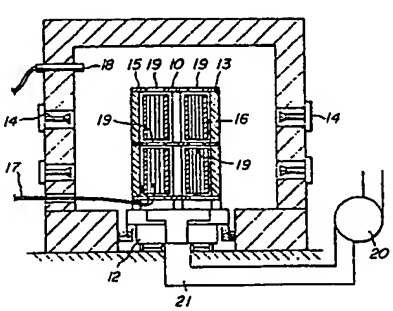
(54) PRODUCTION OF CERAMIC HONEYCOMB STRUCTURE.

(57) This invention provides a method of firing a ceramic honeycomb structure which comprises varying the oxygen concentration in a firing atmosphere in a temperature range where a molding aid and/or a pore forming material is difficultly burnt or in a temperature range where they are burnt, to inhibit abrupt heat buildup of the aid etc., increasing the oxygen concentration in the atmosphere in a temperature range where the pore forming material and/or the molding aid is difficultly burnt to promote their combustion so as to reduce the temperature difference between the internal and external parts of the honeycomb structure, and making uniform the internal and external characteristics without causing any crack inside and at the end parts of the honeycomb structure and without causing internal melt loss. In this manner the method of the invention enables satisfactory firing. Moreover, since it is not necessary to reduce the firing rate, the firing schedule can be shortened and production efficiency can be improved. Accordingly, the present invention is particularly effective or a ceramic honeycomb structure.

FIG. 1



TITLE MODIFIED
see front page

SPECIFICATION

METHOD OF MANUFACTURING CERAMIC HONEYCOMB-STRUCTURAL BODY

(Technical Field)

The present invention relates to a method of manufacturing a ceramic honeycomb-structural body, and more particularly to a method for firing a honeycomb-structural body of ceramic material.

(Technical Background)

Heretofore, it is the common practice in the preparation of a honeycomb-structural body that a green body of ceramic mixture prepared by mixing ceramic material and a molding aids and/or a pore-forming agent is molded firstly to a desired form in a forming mold and then extruded to obtain a desired honeycomb-structural body, thereafter thus-prepared mold is fired in a continuous-feed furnace or in a periodic kiln under a predetermined temperature to attain an ultimate ceramic honeycomb-structural body.

In the firing of such honeycomb-structural body, several admixtures are essentially employed to be mixed into ceramic material, such an organic binder and

a surface-active agent as methyl cellulose, carboxy-methyl cellulose, polyvinyl alcohol, starch paste, wheat flour, glycerol, such a molding aids as wax and the like, and such a pore-forming material as graphite, starch, sawdust and the like, which all exhibit a differential specificity, as reviewed below. More particularly, these molding auxiliaries and pore-forming material may generally suffer from such an inconvenience that they can hardly be heated from the outside of the honeycomb-structural body during the firing operation, while once they are fired, they may be fired abruptly to generate heat, and additionally each of such molding aids has a different ignition temperature. For this reason, there may possibly generate a substantial difference in the temperatures between the interior and the exterior of such a honeycomb-structural body. With such a differential temperature, it is possible that there may generate cracks in the inside or end surface of the honeycomb-structural body or melts in the interior thereof. Also, owing to a substantial difference in the degree of firing of such molding auxiliaries and/or pore-forming agent existing in the interior and the exterior of the honeycomb structure, the properties of such honeycomb-structural body may possibly turn to be ununiform between the interior and

the exterior of the structure (for instance, if a pore-forming agent in a certain area has burned abruptly, it cause a generate irregularly greater pores in the specific area where there is such an abrupt burning). In this respect, therefore, it is generally the practice in the firing operation of such ceramic green body to employ a smaller rate of temperature rising for the purpose of suppressing an abrupt firing in the interior of a ceramic green body in an attempt to prevent from occurring the generation of cracks and interior melts of such green body and the resulted ununiformity between the interior and the exterior in the properties of the fired products. However, with a lower temperature rising in the firing operation, it would cause such a problem that the schedule of operation may naturally be extended, and the efficiency of production may be worse accordingly.

(Disclosure of the Invention)

In view of the foregoing, an object of the present invention is to obviate the above-mentioned such problems by providing an efficient firing process for manufacturing of ceramic honeycomb body.

In the firing process for the manufacture of ceramic honeycomb-structural body in a predetermined atmosphere and at a specified temperature,

an improvement proposed according to this invention is characterized in that the concentration of oxygen in the firing atmosphere may be increased or decreased in connection with the range of temperatures where a molding aids or a pore-forming agent may hardly be fired or where such agents may easily be fired.

According to the present invention, it is arranged such that the concentration of oxygen in the firing atmosphere is increased in the range of temperatures where a molding aids or a pore-forming agent may hardly be burned so that such agents may be forced to be burned on one hand, and the concentration of oxygen in the firing atmosphere is decreased in the range of temperatures where such agents may be fired abruptly so that they may be suppressed from being fired on the other hand, and consequently, there can be attained such advantageous effects that a differential temperature existing between the interior and the exterior of a ceramic honeycomb structure being fired may well be held smaller so that the generation of cracks in the inside and the end surfaces of the structure as well as melts in the interior thereof may efficiently be prevented from occurring, and that the fired product may turn to be uniform in the quality and properly throughout all its portions, the interior or

exterior. Moreover, as it is not required to make the rate of temperature rising smaller during the firing operation, the efficiency in production can then be made better accordingly.

(Brief Description of the Drawing)

Fig. 1 is a cross-sectional view showing generally the construction of a periodic kiln used for the practice of a firing process according to the present invention.

10: a sample; 11: a periodic kiln; 12: a carriage; 13: a receiving plate; 14: a furnace burner; 16: a direct fire shield plate; 17: a thermocouple; 18: an oxygen sensor

(Best Mode for Carrying out the Invention)

In preparation of the firing of a ceramic honeycomb-structural body to be manufactured according to the present invention, firstly, ceramic material of a desired grain size is mixed homogeneously and this is then admixed with a molding aids and/or a pore-forming agent to obtain a plasticized batch of moldable ceramic mixture, thus-prepared batch of plasticized mixture being subjected to the extrusion step to be molded to a desired shape, thereafter being dried to be a thus-molded body ready to be fired in a furnace. Next, in the following step of firing, it is arranged according

to the present invention such that the current concentration of oxygen in the firing atmosphere is adjusted accordingly to a differential temperature between the interior and the exterior of the molded body which is being measured during the firing operation, so that the degree of burning of molding aids and pore-forming agent may be controlled, and so that the prepared molded body may be fired optimally to obtain a desired ceramic honeycomb-structural body. For this arrangement, there are provided at least two thermocouples in appropriate positions of the interior and the exterior of a specific molded article to be fired for the purpose of measuring a differential temperature therebetween. This differential temperature to be measured between the interior and the exterior of the molded material by such thermocouples may be either a positive value or a negative one. A positive value of differential temperature represents that a temperature in the interior is lower than that in the exterior of the article out of the range of temperatures that a molding aids and a pore-forming agent may be burned, while a negative value represents that an interior temperature is higher than an exterior temperature of the article owing to heat generated from such admixed agents in the temperature range that they are being

burned, respectively. More specifically, the measuring of a differential temperature is adapted to capture a range where the sense of differential temperature may change, namely, either from the positive to the negative or *vice versa* to appropriately control the current concentration of oxygen in the firing atmosphere.

In practice, the control of such a concentration of oxygen in the atmosphere may be considered by way of the following means.

1) For increasing the current concentration of oxygen in the furnace:

① increasing the air-fuel ratio in a furnace burner by the introduction of an increased diffusion rate of air.

② adding the current percentage of oxygen gas in the combustion gas to be fed to the burner.

2) For decreasing the current concentration of oxygen in the furnace:

① decreasing the air-fuel ratio in a furnace burner by decreasing the current quantity of combustion gas fed to the burner.

② adding nitrogen gas to the combustion gas to be fed to the burner.

Additionally, for the accurate control of the current concentration of oxygen, an oxygen sensor is

provided in an appropriate position in the atmosphere of the furnace. Also, in consideration of the fact that as a pore-forming agent is admixed thoroughly in the molded ceramic body, it has generally a limited chance to contact with oxygen in the firing atmosphere so that it is rather hard for it to be fired during the firing operation, and that once it is fired, it can hardly be extinguished, it is then preferred to provide the firing atmosphere with an excessive concentration of oxygen.

In practice, it is preferable to employ an appropriate molding aids selected from the group consisting of an organic binder, a surface-active agent, waxes, such as, for example, methyl cellulose, carboxy-methyl cellulose, poly(vinyl alcohol), starch paste, wheat flour, glycerol, and an appropriate pore-forming agent selected from the group consisting of graphite, starch, sawdust.

Example 1

Ceramic materials such as kaolin and alumina are prepared to be mixed together in an appropriate mixing ratio to obtain mullite composition, to which glycerol or a surface-active agent is admixed as a molding aids, which is to be plasticized, molded and then dried in the following steps for attaining a desired molded article. Thus-prepared molded article 10 was put onto a top plate

13 positioned on a traveling carriage 12, which is movable through the interior of a tunnel furnace 11, in the manner as shown in Fig. 1, and then subjected to the firing operation under the conditions shown in Table 1. In the firing operation, while a plurality of burners 14 mounted in the opposed side walls of the furnace were provided as heating means, it is preferred that solid shield plates 16 made of mullite-contained material are arranged in position between outer posts of the top plate 13 so that a plurality of prepared shaped articles or ceramic honeycomb-structural body 10 is not subjected directly to firing from the burners.

Also, there were provided two thermocouples 17 at appropriate positions in the inside and the outer surface of one of the prepared shaped articles 10 disposed within the tunnel furnace 11, and further, an oxygen sensor 18 was placed in the side wall of the furnace in such a manner that its sensing head extends there through into the interior space of the furnace 11.

Preferably, it may be arranged such that there are provided a plurality of openings 19 in receiving plates 15 which oppose each of the honeycomb-structural body 10 disposed thereupon so that the atmosphere of the furnace may be assisted to pass efficiently through the interior of the honeycomb-structural body 10, and also

provided an exhaust passageway 21 extending through the carriage 12 and the furnace bottom to an exhaust blower for directing a mass of atmosphere to the outside so that no substantial difference in temperatures may exist between the interior and the exterior of the honeycomb-structural body.

With this arrangement, the furnace atmosphere was heated to the maximum temperature of 1400°C and held at this temperature for two and half hours with the prepared shaped article disposed in position, and then cooled at the cooling rate of 150°C/hr.

The results obtained from this firing operation is shown in Table 1.

Table 1

Sample No.		Product by the invention		Reference product
		1	2	3
Composition of fired product		Mullite	Mullite	Mullite
Starting material		Kaolin & Alumina	Kaolin & Alumina	Kaolin & Alumina
Molding aids		Glycerol	Surfactant	Glycerol
Pore-forming agent		None	None	None
Temperature rising rate (°C/hr)	100~ 500°C	65	65	50
	100~1200°C	100	100	100
O_2 Concentration (%)	200~ 300°C	10	10	19
	500~ 800°C	15	15	15
	800~1000°C	12	12	12
Range where differential temperature between product in & out is negative (°C)	When molding aids fired	200~400	150~350	200~300
	When pore-forming agent fired	None	None	None
Absolute differential temperature under above condition (Max) (°C)	When molding aids fired	20	30	100
	When pore-forming agent fired	None	None	None
Crack generating rate (%)		0	0	55
Interior melts generating rate (%)		0	0	0
Difference in bores in/out product (μ)		0.5	1.0	0.5
Evaluation		○	○	×

As is evaluated from Table 1, in the case that the oxygen concentration in the furnace atmosphere is not controlled as in the conventional manner, it is found that the differential temperature between the interior and the exterior of the molded shaped article turned to be a negative value in the range of temperatures from 200 to 300°C owing to heat generated from the fired molding aids, and that its absolute differential temperature was as large as 100°C maximum. In contrast, however, with the Samples Nos. 1 and 2 processed with the oxygen concentration of 10% in that range of temperatures according to the present invention, it is noted that the negative range of temperatures were from 200 to 400°C and from 150 to 350°C respectively, and also its absolute differential temperature was as small as 20°C and 30°C maximum, respectively.

From the visual check-up of thus-fired products processed under such conditions for the crack generation rate (%), the interior melt generation rate (%) and the difference in bores formed in the interior and the exterior of the products (μ), it is observed that the products according to the present invention turned out with no generation of cracks, in contrast to the case of a product compared with the crack generating rate of 55%.

Example 2

Ceramic materials such as talc, kaolin and alumina are prepared to be mixed together with an appropriate mixing ratio to obtain cordierite composition, to which mixture starch paste or methyl cellulose is admixed as a molding aids, and further with sawdust or graphite as a pore-forming agent, which is to be plasticized, molded and then dried in the following steps for attaining a desired molded shaped article. Thus-prepared shaped article was mounted onto the receiving plate in the interior of a tunnel furnace 11 in the same manner as in the Example 1, and then subjected to the firing operation under the conditions shown in Table 2. In the firing operation, the furnace atmosphere was raised to the maximum temperature of 1350°C and held at this temperature for six hours with the prepared shaped article disposed in position, and then cooled off. The results obtained from this firing operation is shown in Table 2.

Table 2

Sample No.		Product by the invention		Reference product
		1	2	3
Composition of fired product		Cordierite	Cordierite	Cordierite
Starting material		Talc, Kaolin & Alumina	Talc, Kaolin & Alumina	Talc, Kaolin & Alumina
Molding aids		Starch paste	Methyl cellulose	Starch paste
Pore-forming agent		Sawdust	Graphite	Sawdust
Temperature rising rate (°C/hr)	100~ 500°C	80	90	60
	100~1200°C	100	115	60
O_2 Concentration (%)	200~ 300°C	8	6	18
	500~ 800°C	21	21	15
	800~1000°C	10	9	12
Range where differential temperature between product in & out is negative (°C)	When molding aids fired	200~400	200~400	200~300
	When pore-forming agent fired	500~1000	500~1000	600~900
Absolute differential temperature under above condition (Max) (°C)	When molding aids fired	25	15	120
	When pore-forming agent fired	30	20	80
Crack generating rate (%)		0	0	75
Interior melts generating rate (%)		0	0	30
Difference in bores in/out product (μ)		2	0.5	15
Evaluation		○	◎	×

As is evaluated from Table 2, in the case of products to be compared that the concentration of oxygen in the furnace atmosphere is not controlled as in the conventional manner, it is found that the differential temperature between the interior and the exterior of the molded shaped article turned to be a negative value in the range of temperatures from 200 to 300°C and from 600 to 900°C, and that its absolute differential temperature was 120°C and 80°C maximum, respectively. Also, it is observed that the differential temperature turned to be a positive value in the range of temperature from 500 to 800°C, and that its absolute differential temperature was 80°C. In contrast, however, with the Samples Nos. 1 and 2 processed with the oxygen concentration of 8 and 10%; and 6 and 9% in those ranges of temperatures turning to a negative value according to the present invention, it is noted that their absolute differential temperatures turned out to be 25°C and 30°C; and 15°C and 20°C maximum, respectively. Also, with the oxygen concentration of 21% in the furnace atmosphere in the range of temperatures where the differential temperature turned to be a positive value, its absolute differential temperature turned to be 50°C.

From the visual check-up of thus-fired products processed under such conditions for the cracks

generation rate (%), the interior melts generation rate (%) and the difference in bores formed in the interior and the exterior of the products (μ), it was observed that the products according to the present invention turned out with such a small order of dispersion of bores as of 2 and 0.5 μ, respectively, in contrast to the case of a product compared with the difference in bores turned to be as large as 15 μ.

While the invention has been described by way of its preferred embodiments with a certain degree of particularity, it is to be understood that the invention is not restricted to the details of such embodiments, but various changes and modifications may be made in the invention by those skilled in the art without departing from the spirit and scope thereof.

(Effect of the Invention)

As is apparent from the detailed description presented hereinbefore, according to the firing process for the manufacture of a ceramic honeycomb-structural body of the present invention, the abrupt heat generation of a molding aids and/or a pore-forming agent admixed to a ceramic material may be suppressed by decreasing the oxygen concentration in the firing atmosphere in the range of firing temperatures for such an admixed agent on one hand, and in reverse the firing

of such an admixed agent may be facilitated by increasing the current concentration of oxygen in the firing atmosphere in the range of temperatures where such an admixed agent can hardly be fired on the other hand, thereby to afford a substantial decrease in a differential temperature existing between the interior and the exterior of the burned honeycomb-structural body, which may consequently effect the prevention of cracks in the inside or in the end surface of such a product or interior melts thereof from being generated, and which may contribute to the attainment of uniformity of the specific properties in the interior and the exterior of such a product, whereby an optimal firing may be afforded, accordingly.

Moreover, since it is not required to make the temperature rising rate smaller during the firing operation, the schedule of firing operation can be made shorter, the efficiency in production can then be made better accordingly.

Claims

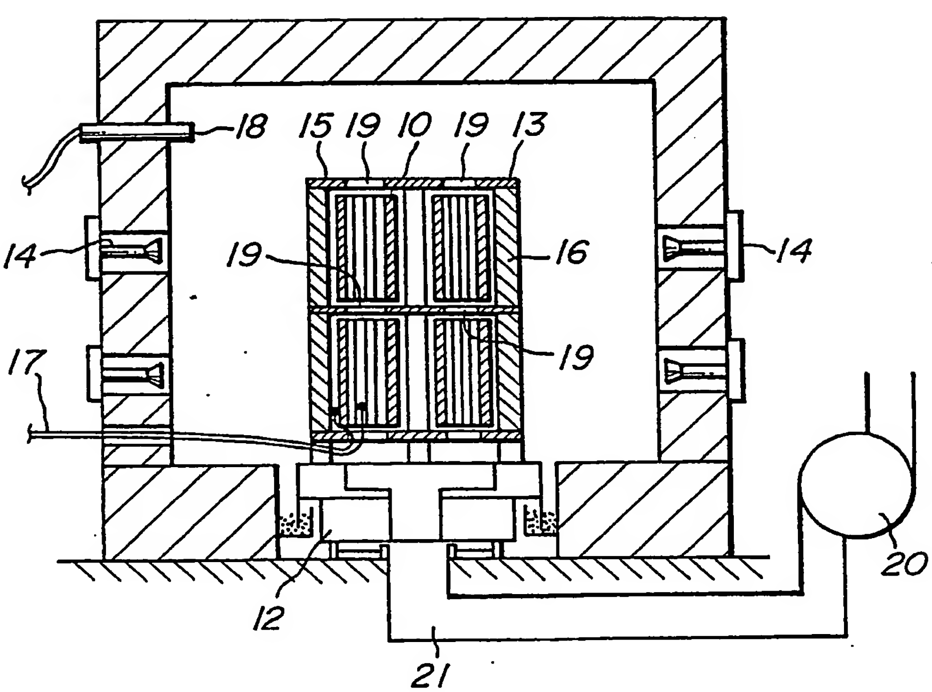
1. A process of producing a honeycomb-structural body comprising:

mixing a ceramic material with an element selected from group consisting of a molding aids and a pore-forming agent, preparing a green ceramic material, extruding the thus prepared green material to form a desired honeycomb-structural body and firing, wherein said molding aids and a pore-forming agent is removed by firing with the control of oxygen concentration in the firing atmosphere.

2. A process as defined in claim 1, wherein the oxygen concentration in the firing atmosphere is made greater in the range of firing temperatures which is in accordance with the temperature of thermal decomposition of said pore-forming agent.

3. A process as defined in claim 1, wherein the oxygen concentration in the firing atmosphere is made smaller in the range of firing temperatures which is in accordance with the temperature of thermal decomposition of said molding aids.

FIG_1



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/00139

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

$Int.Cl^4$ C04B38/00, C04B35/64

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	C04B38/00, C04B35/64

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho	1926 - 1988
Kokai Jitsuyo Shinan Koho	1971 - 1988

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	JP, A, 54-138005 (NGK Spark Plug Co., Ltd.) 26 October 1979 (26. 10. 79) Page 1, left column, lines 5 to 16 and page 2, lower left column, lines 10 to 17 (Family: none)	1
A	JP, A, 55-144474 (TDK Electronics, Co., Ltd.) 11 November 1980 (11. 11. 80) Page 1, left column, lines 6 to 12 (Family: none)	2, 3

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
March 17, 1989 (17. 03. 89)	April 3, 1989 (03. 04. 89)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	